Photochemical Transformations of the Structural and Optical Properties of Marine Colored Dissolved Organic Material in Coastal Waters

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LONG-TERM GOALS

My long-term goals are to develop an understanding of the photochemical processes affecting CDOM, and the resultant changes in its optical properties and molecular composition, in coastal environments.

OBJECTIVES

I am now starting the third year of a tenure track position at Chapman University after being a research assistant at RSMAS, U. of Miami. This is the second year of a small two year grant to facilitate setting up my new research program and bringing to a closure collaborations with Rod Zika's research group at RSMAS. My objectives for this year were to: 1) organize and cochair a special session on results from recent ONR-funded cruises at the 2002 Ocean Sciences meeting; 2) complete and publish a paper on cruise data from the ONR-funded cruises in the Gulf of Mexico in 1999/2000 with Rod Zika in a special issue of *Marine Chemistry* covering the Ocean Sciences special session; 3) accumulate water samples from a range of local and national fresh vs. marine sites through sample exchange with other groups; 4) complete a collaboration on FFFF and LC/MS studies with Rod Zika's group at RSMAS.

APPROACH

In collaboration with Dr. Rod Zika, Eliete Zanardi and Erik Stabenau (graduate students) at RSMAS, our approach to CDOM characterization is to use Flow Field Flow Fractionation (FFFF) as the separation technique, together with optical characterization of fractionated CDOM by in-line absorbance and fluorescence and structural characterization by ion trap mass spectrometry (LC/MS^n). In the first year of this grant, FFFF studies on a series of riverine and marine DOM samples from South Florida waters were completed, along with photochemical studies to see if irradiation of fresh CDOM produces material with the same structural and optical characteristics as marine CDOM. In the second year, these experiments have been extended to LC/MS through an exchange of samples. A range of Gulf of Mexico coastal and blue water samples were collected on multiple cruises by Dr. Bob Chen, U. Mass. Boston and Rod Zika, RSMAS. Local field studies and sampling of southern California salt marshes and coastal waters continue to be carried out within a larger multidisciplinary on-going research project led by Dr. Stanley Grant (UCI).

WORK COMPLETED

As planned, I co-convened and co-chaired a one and a half day special session titled "CDOM in the Coastal Ocean: Transformation Processes and Their Effects on Optical Properties" at the National

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Ocean Sciences meeting (February 2002, Honolulu). My co-conveners were Dr. Paula Coble (USF) and Dr. Rod Zika (RSMAS). This session served as a focused venue for results from the many ONR-funded cruises and studies over the last few years that have addressed these questions. There were 42 national and international presenters in the session. A special issue of *Marine Chemistry* is planned for 2003 publication to cover this session. I was a co-presenter on one talk and three posters at this meeting:

E. Zanardi-Lamardo, C. D. Clark, R. G. Zika, "Molecular Mass Distribution and Characterization of Coastal Waters in Southwest Florida", National Ocean Sciences Meeting, Honolulu, February 2002.

S. Jakubowski, L. Litz, C. D. Clark, J. Li, S. Grant, "Variability of Hydrogen Peroxide, a CDOM Photochemical Product, in a Surf Zone", National Ocean Sciences Meeting, Honolulu, February 2002.

D. E. Wellman, C. D. Clark, D. M. Foley, S. B. Grant, "Diurnal Photochemical and Biological Processes of CDOM in Southern California Coastal Waters", National Ocean Sciences Meeting, Honolulu, February 2002.

L. Litz, E. Morey, S. Jakubowski, C. D. Clark, S. B. Grant, "Sources and Optical Properties of CDOM in a Southern California Salt Marsh", National Ocean Sciences Meeting, Honolulu, February 2002.

A library of coastal water samples is been accumulated in this laboratory for future optical and structural studies. Samples were collected on three cruises in the coastal waters of the Gulf of Mexico. In April 2001, Bob Chen took samples in the Mississippi River. In September and November 2001, Cindy Moore took samples for us on a cruise from RSMAS up the west coast of Florida, revisiting the sites from the large ONR-funded multi investigator cruise in June 2000. These samples have all been analyzed here for optical and physical properties, and some samples have been concentrated by ultrafiltration in preparation for follow-up experiments on photochemical and structural properties.

Local coastal and salt marsh water samples have also been taken from several systems. In June/July 2001, I participated in a large study of the waters of two salt marsh systems (Newport and Oxbow Sloughs) that drain into the surf zone at Huntington Beach, and may impact beach quality in this area. Huntington Beach is frequently closed due to high bacterial counts, which may originate in the marshes from birds or anthropogenic inputs i.e. sewage leaks. The salt marshes are completely isolated well-defined systems with no freshwater inputs, and hence only local CDOM production sources. My interest was in any potential differences between CDOM in the incoming tides (coastal seawater) vs. the outgoing tides (salt marsh water) due to different sources. The salinity, absorbance and 3D fluorescence of these samples were measured. A series of the ten most prevalent plant species from these sites were sampled in July 2002. 3D-EEMS were measured for the plant leachates to identify the different end-members, and photochemical irradiation experiments were performed. In addition, I participated in a field study at Doheny State Beach in April 2002, examining CDOM inputs and optical properties in this local estuary.

Over 2001/2002, FFFF studies on CDOM in two South Florida fresh to marine transition zones were completed. Size separation in FFFF relies on the molecular diffusion coefficient i.e. molecular size, and offers some advantages compared to other common DOM fractionation techniques that suffer from charge adsorption and charge repulsive effects. FFFF was applied to DOM samples from the Shark and Caloosahatchee Rivers in Southwest Florida. Two papers were published on this work: one on the methodology for CDOM in natural waters (2001), and one on the differences in CDOM between the

two rivers and fresh to marine waters (2002). I have recently exchanged local wetland and plant leachate end-member samples with Erik Stabenau of the RSMAS group for LC/MS studies on structural correlations with optical properties among these samples. We anticipate one joint manuscript from this work within the next year.

RESULTS

Studies are reported here for a local coastal water system. The Santa Ana River, the largest stream system in Southern California, serves as the primary drainage basin for the urbanized area of Orange County. Three locations in Huntington Beach, California, located along the eastern side of the Santa Ana River channel, were sampled June 26-July 21, 2001. In the summer months, there is little to no freshwater flow in the Santa Ana River. Station W5 was located in the Newport Slough, a salt marsh, inside the tide gate to the Santa Ana River. Station W4 was located at the tide gate in the Oxbow slough, further downstream from the Newport Slough. Station W2 was located 100 feet from where the Santa Ana River empties into the surf-zone at Huntington Beach. For six tidal cycles, samples were taken from W2, W4 and W5 at the peak of the flood tide, just after the flood tide, and at the lowest point of the ebb tide. The hypothesis was that salt marshes are a source of both CDOM and bacteria from birds to the surf zone.

Salinity was fairly constant at 31-33. The absorbance spectra obtained for all water samples were characteristic of CDOM, with an exponential decrease in absorbance from 250 to 500 nm. The absorbance at 300 nm (taken as an approximate measure of the CDOM level) was anti-correlated with the tidal processes, with the maximum absorbance measured at ebbing tide and the minimum at flood tide (differences of a factor of 2-4). Absorbances were consistently 30-50% higher at the Upper and Lower Sloughs than at the SAR outlet. This indicates that the Sloughs are a source of colored dissolved organic carbon to the surf zone, with high-CDOM containing waters pulsing out of the slough on an ebbing tide and dilution by low-CDOM containing waters on a flooding tide. Covariant analyses of different wavelengths in UV/VIS spectra have been previously used to differentiate between marine vs. terrestrial derived CDOM, as well as between freshly produced vs. more degraded material. A co-variant analysis of the absorbance at 254 nm vs. 300 nm gave a linear plot, suggesting that most of these samples likely have the same source of CDOM. However, one sample at the SAR outlet at flood tide indicated a contribution from a different source of CDOM. This was associated with a cold-water upwelling event on 28 June, and may be due to a marine-derived CDOM source.

Typical 3-D excitation-emission matrix (EEM) fluorescence spectra for the SAR outlet and the Lower Slough are shown in Figure 1. EEMs for the Upper and Lower Sloughs at ebb tide were in general characteristic of freshly produced CDOM from terrestrial plant degradation processes in the wetlands, with terrestrial humic peaks A and C present along with protein peak T. A similar signal is observed at the SAR outlet (W2) at ebb tide, but the humic peak is higher. By contrast, on a flood tide, significantly lower fluorescence intensities were measured (a factor of 10-20 lower). This indicates that low-CDOM containing waters are flooding in from the coastal ocean. However, the EEMs are still characteristic of degraded terrestrially derived material. Based on the prevailing long-shore currents during the study period, the CDOM in the coastal waters likely derived from diluted inputs from other local wetland systems, such as down coast Newport Back Bay. In association with two cold-water upwelling events and a subsequent phytoplankton bloom (28 June and July 8 onwards), a marine CDOM signal (peak M) was observed at the SAR outlet on the flood tides.

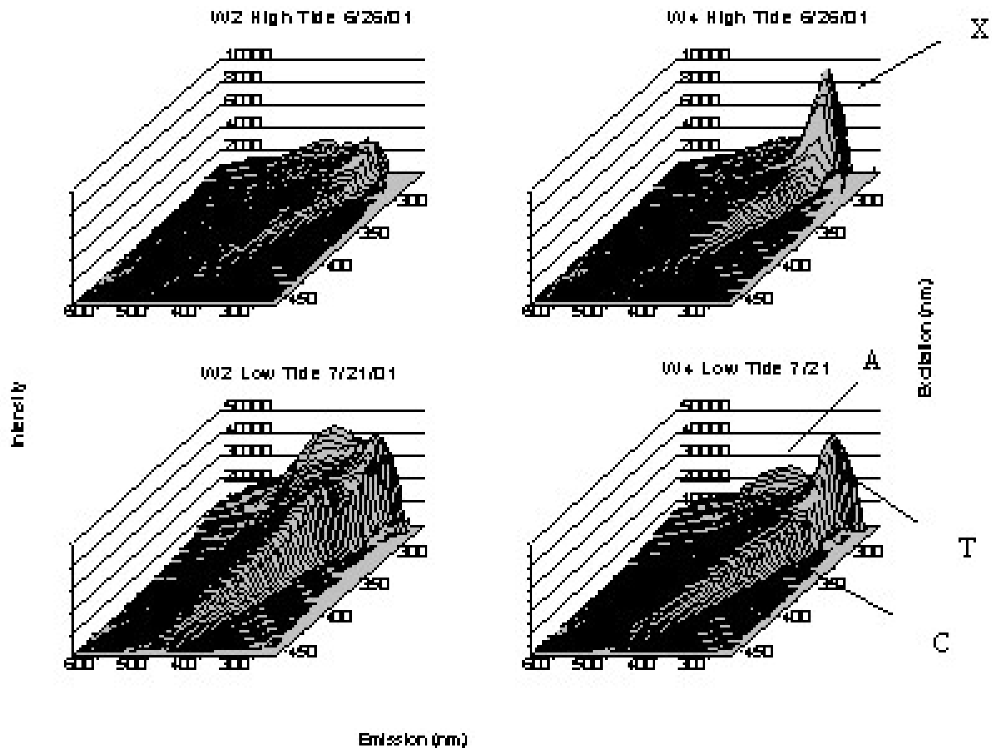

Figure 1. Typical 3D Excitation-Emission Matrix (EEM) fluorescence spectra at Stations W2 (Santa Ana River outlet) and W4 (lower slough). Note 5 x lower intensity scale for flood vs. ebb tide. [Peaks A and C: terrestrial humics and Peak T: protein – present at both W2 and W4 at ebb tide; Peak X: salt wort leachate (grows along slough banks at W4, which are only submerged at flood tide)- present only at W4 at flood tide]

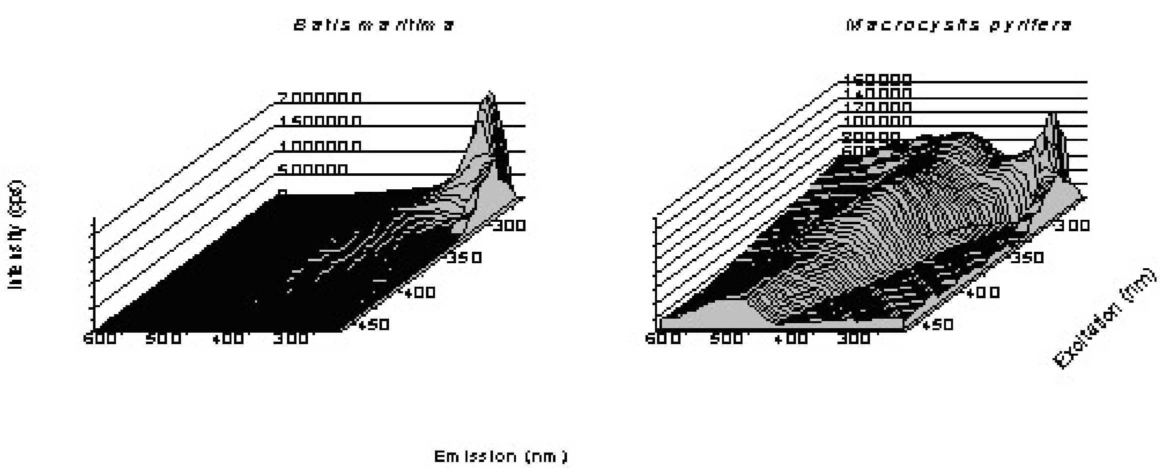

Figure 2. 3-D Excitation-Emission Matrix (EEM) fluorescence spectra for salt wort (LHS) vs. brown seaweed (RHS) leachates before photodegradation. [Only the protein-like peak is present for salt wort, but brown seaweed has both protein-like and humic-like peaks]

Salt marsh plants dominant at the study site were collected to investigate the optical properties of the CDOM produced and how it degraded with exposure to sunlight. Specimens included saltbush (*Atriplex lentiformis*), pickelweed (*Salicornia virginica*), sea fig (*Carpobrotus chilensis*), salt wort (*Batis maritima*), alkali health (*Frankenia grandiflora*), and brown seaweed (*Macrocystis pyrifera* - found on the sampling station tide gates). Plant leachates were analyzed for optical properties and irradiated to measure photochemical effects. Figure 2 shows EEMs for salt wort and brown seaweed before photodegradation had taken place. Most of the local wetland plants produced only proteinaceous material, but two species produced humic type substances characteristic of CDOM fluorescence. Resistance to photodegradation was dependent on plant type. Most species showed significant degradation of the protein peak by 28 hours of sunlight exposure. This is about twice as long as the residence time in the wetlands. Organic matter from salt wort was markedly more recalcitrant to photodegradation, and may have a longer lifetime within the salt marsh system. The combined fluorescence signals from the plant leachates were readily observable in the wetland outputs. A manuscript is in preparation for submission to *Env. Sci. and Tech.*

IMPACT/APPLICATIONS

Identification of the optical properties of end-members in various ecosystems is required to constrain models of CDOM optical properties in the coastal ocean by defining the optical properties of the inputs by geographic region. One method is through plant leachate studies of dominant species in a variety of important ecosystems eg. agricultural, native wetland, tropical, desert. This study focused on a Pacific salt marsh in a Mediterranean climate, but these methods could be applied to a wide range of other systems. Isolated wetland systems like this study site provide a unique opportunity to examine a series of discrete end-members and their combined contributions to the overall optical properties of the waters input to the coastal ocean.

TRANSITIONS

The optical data collected in the local sloughs and Doheny State Beach have been used by Drs Stan Grant (UCI), Jim Noblet (SCCWRP) and Denise Foley (Chapman University) in their analyses of potential sources of changing bacterial levels in the water.

RELATED PROJECTS

In a related ONR YI grant, I am examining the effect of quinone moieties on the photochemistry of CDOM in coastal waters. Specifically, I am using NMR techniques for structural characterization, along with measurements of photochemical products, to correlate specific structural features with enhanced photochemical activity and determine if quinone functionalities are the key feature in CDOM that absorbs sunlight and produces transient products such as peroxide.

In a multi-investigator project recently funded by the NSF, I have incorporated GIS and field studies of the Upper Newport Back Bay, an ecological reserve, into undergraduate geoscience courses. This will provide additional opportunities for collecting different source waters.

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